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Hanford Waste-Form Release and Sediment Interaction

A Status Report with Rationale and Recommendations for Additional Studies

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successful competitor with cobalt for sorption sites. Sorption R_d for cobalt decreased from 3400 to 200 mL/g as calcium concentrations increased from 2 x 10^{-3} to 2 x 10^{-1} M. On the other hand, cobalt R_d increased with increasing sodium and potassium concentrations (from 2100 to 4700 mL/g as Na increased from 1 x 10^{-3} to 3 M, and from 500 to 3400 mL/g as potassium increased from 2 x 10^{-3} to 2 x 10^{-1} M). These data clearly indicate that the cation exchange process is not the only process affecting cobalt sorption. The authors suggested that colloid formation and physical sorption were occurring. Conversely, Barney (1978) observed that the sorption of cobalt on Hanford soil was reduced in the presence of potassium. Specific R_d values were not reported.

Some field studies and laboratory studies on Hanford soil indicate that cobalt readily reacts with organic and inorganic anions when they are present at high concentrations. These observations are supported by other studies on soils similar to Hanford soil. Haney (1967) reported the occurrence of cobalt in groundwater under the 216-BY crib. He proposed that the apparent high mobility of cobalt in the soil column was due to the formation of anionic cobalt phosphate complexes resulting from the high phosphate content in the waste stream. Barney (1978) observed that the sorption of cobalt on Hanford soil was reduced in the presence of nitrite (NO_2) and humic acid, presumably because of the formation of anionic or neutral complexes with cobalt. Wilding and Rhodes (1963) demonstrated that the addition of EDTA to a soil water system would reduce the cobalt R_d by a factor of 100.

Based on the foregoing information, the recommended range of sorption R_d for cobalt is 500 to 2000 mL/g for ambient Hanford soil conditions (neutral to slightly basic pH, low ionic strength, and low organic content). A recommended range for high-salt, high-organic, and/or -acid conditions cannot be specified with any confidence because of the lack of data. General indications are that R_d values will be much lower under these conditions.

3.3.7 <u>Uranium Data</u>

Under oxidizing conditions (typical for Hanford), dissolved uranium is predicted to exist as a cation (UO_2^*) up to a pH of approximately 6, as a neutral hydroxide species $UO_2(OH_2)^8$ from a pH of approximately 6 to 8, and as an anionic carbonate $UO_2(CO_3)^{\frac{4}{3}}$ above a pH value of 8. Uranium may also complex with other

anions (e.g., fluoride, chloride, and phosphate) to form neutral or anionic species, but such complexes should not exist in significant concentrations under ambient Hanford groundwater conditions. These estimated species distributions suggest that uranium would sorb via cation exchange under acid conditions and sorb very poorly under neutral and basic conditions.

No laboratory studies have been published describing uranium sorption in Hanford soil, but unpublished work (Wayne Martin at PNL) and U1/U2 pond experience (Delegard et al. 1986) suggest uranium is not adsorbed under ambient Hanford groundwater conditions and slightly acidic conditions, respectively. Characterization of 300 Area soil underneath the 316-4 crib by Ames and Phillips (1979) indicates that uranium is rather immobile because of solubility constraints rather than sorption. Strong evidence is presented that a uranium phosphate has precipitated because of the high phosphate content in the waste stream. Leaching experiments were completed as part of the study and showed that 0.1 N HNO3 acid was very successful at removing uranium from the contaminated soil column while distilled water and a methyl isobutyl ketone solution did not remove uranium from the soil. The data indicate that nitric acid dissolves the uranium phosphate phase.

General indications are that uranium sorption values will be low under most circumstances because uranium tends to form neutral or anionic species at neutral or basic pH values and is a poorly adsorbing cation at acid pH values. We recommend more data be collected on U adsorption from waste leachates and groundwater onto Hanford sediments.

3.3.8 Ruthenium Data

Thermodynamic data that predict aqueous speciation of ruthenium are largely unknown. Available data indicate that ruthenium exists primarily in the +3 and +4 oxidation states and is rarely, if ever, a simple cation. Ruthenium readily complexes with common anions (hydroxide, nitrate, nitrite, chloride) and may form a variety of anions or cations depending on the given chemical system. Consequently, ruthenium sorption is highly variable and predictions of expected sorption ranges are quite sensitive to a particular waste stream. Rhodes (1957a) investigated ruthenium sorption on Hanford soil as a function of pH. Ruthenium was introduced into solution as ruthenium chloride (RuCl₃). Maximum sorption occurred in the pH range 4.7 to 8.5 (R_d 101 to 274 mL/g)